

# Strength and High-Temperature Stability of Dispersion Strengthened Nickel-MgO Alloys

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*Nickel powders of 1-, 0.4-, and 0.2- $\mu$  average particle size were combined with 0.05- $\mu$  MgO powder. Oxide was added in quantities of 4, 12, and 20 vol pct. The mixtures were vacuum hot pressed and extruded at 2100°F. In spite of a general tendency to growth of oxide particles during processing, dispersions of fineness comparable to those of Sintered Aluminum Powder, SAP, were achieved. A small amount of oxide considerably improved 1800°F stress-rupture strength, but further oxide addition resulted in a decrease of strength.*

RECENTLY there has been much speculation concerning the requisites for strong and stable dispersion-strengthened alloys. The nature of the dispersed phase, the stability of the alloys, and variables influencing the mechanical properties of alloys have been given consideration. Such topics have been reviewed by Bunshah and Goetzel.<sup>1</sup>

Of the many parameters related to the mechanical properties of dispersion alloys, mean free path between dispersed particles (a measure of the fineness of the dispersion), particle size, and vol pct of the dispersed phase have been shown to be very important. Generally, strength increases with decreasing mean free path, and there is an optimum vol pct of dispersed phase.

Just how fine a dispersion ought to be is somewhat open to debate, but Irmann,<sup>2</sup> Lenel, Backensto, and Rose,<sup>3</sup> Gregory and Grant,<sup>4</sup> and others have shown in the original SAP-type alloys, aluminum plus aluminum oxide alloys, that better strength is generally obtained with finer dispersions and the best strengths were obtained when the mean free path was less than 1 $\mu$ . Further, Cremens, and Grant<sup>5</sup> showed that in nickel plus aluminum oxide alloys, stress-rupture strength at 1500°F was definitely increasing with decreasing mean free path. In their investigation, however, the finest dispersions that were produced were about 2.0 $\mu$  mean free path. To determine the potential of the nickel plus oxide type of product, it would be neces-

sary to obtain dispersions analogous to those of SAP alloys; namely, ones where the mean free path between oxides is less than 1 $\mu$ .

Unfortunately, however, it is very difficult to produce extremely fine dispersions of oxides in metals other than those which naturally form refractory oxide skins. There are several approaches to this problem including such procedures as mechanical mixing, internal oxidation, reduction of mixed oxides, and metal deposition from solution.

Work at the Lewis Research Center has shown that metal powders 0.1 $\mu$  or finer could be produced by ball milling, when selected grinding aids were utilized.<sup>6</sup> Because these unusually fine powders were available, it was an initial objective of this study to determine if by mixing of these fine Ni powders with various amounts of MgO (0.05 $\mu$ ) a fine dispersion of MgO in Ni comparable to those in Al-Al<sub>2</sub>O<sub>3</sub> might be achieved. A second objective was then to attempt to relate the parameters of structure to 1800°F stress-rupture strength of the alloys.

Nickel powders of 1-, 0.4-, and 0.2- $\mu$  average particle size were combined with 0.05- $\mu$  average particle size MgO powder. This oxide was added in quantities of 4, 12, and 20 vol pct. The mixtures were hot pressed and extruded at 2100°F.

Table I. Distribution of MgO in Ni after Processing

[Initial MgO size, 0.05 $\mu$ ]					
Size Ni Powders, $\mu$	Vol Pct MgO <sup>a</sup>	Lineal Analysis Results from Electron Micrographs			Stress for 100 Hr Rupture Life, psi <sup>b</sup>
		Vol Pct Oxide	Mean Free Path, $\mu$	Average Oxide Particle Size, $\mu$	
1.0	0	—	—	—	620
	4	6.8	2.11	0.20	3170
	12	13.7	1.40	0.21	2060
	20	19.5	1.28	0.39	—
0.4	0	—	—	—	620
	4	10.7	1.22	0.18	3260
	12	11.8	0.70	0.06	2150
	20	23.0	1.15	0.38	1320
0.2	0	—	—	—	620
	4	8.0	1.89	0.21	2750
	12	20.5	1.12	0.31	1120
	20	28.1	1.18	0.64	710

<sup>a</sup> Volume percent MgO added to alloys.

<sup>b</sup> Data from curves in Fig. 3.

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Table II. Chemical Analyses of Materials

International Nickel Company Carbonyl "B" Nickel Powder <sup>a</sup>	
Element	Wt Pct
Ni	99.79
Fe	0.008
C	0.09
O <sub>2</sub>	0.11
S	Nil
Baker Analyzed Reagent Magnesium Oxide <sup>b</sup>	
MgO	98.6
-Cl	0.005
-NO <sub>3</sub>	0.005
-SO <sub>4</sub>	0.002
Ba	0.005
Mn	0.004
Ca	0.02
Heavy metals (as Pb)	0.002
Fe	0.003

<sup>a</sup> Analysis supplied by supplier.  
<sup>b</sup> Typical analysis.

## EXPERIMENTAL

The specimens for this investigation were prepared from nickel and magnesium oxide powders by milling, mixing, washing, drying, hydrogen cleaning, cold pressing, and vacuum hot pressing of the powders with subsequent canning and extrusion of the hot-pressed billets. Table I lists the alloys so prepared.

International Nickel Company "Carbonyl B" nickel powder, 2.5- $\mu$  particle size, and Baker Analyzed Reagent Magnesium Oxide, 2.0- $\mu$  particle size, were used as starting materials. Chemical analyses are shown in Table II. Special precautions were used throughout the specimen preparation to avoid oxygen contamination since it was known that the nickel powders oxidized readily when exposed to oxygen and in some cases were pyrophoric in air.

To reduce the size of the nickel and MgO powders, they were premilled in a Szegvari Attritor Mill in *n*-heptane with 2 pct oleic acid\* under argon atmos-

\*Wt pct acid determined on the basis of weight of powder charge.

phere and then were mixed in this same mill. The nickel powders were milled for 10, 24, or 72 hr depending upon whether 1.0-, 0.4-, or 0.2- $\mu$  powders were desired. If oxide was added, it was done 5 hr prior to the end of these milling periods. The MgO had been pre-milled for 72 hr in the attritor mill in *n*-heptane with 2 pct oleic acid to produce 0.05- $\mu$  average particle size powder. After milling and mixing, the powders were washed on Buchner funnels and dried in vacuum at room temperature. The powders were then hydrogen cleaned for 4 hr at 650°F in purified hydrogen in an attempt to reduce nickel oxide that had been formed as an impurity and to drive off from the powders any volatile adsorbed material.

The cleaned powders were subsequently handled under argon or vacuum where possible. This was accomplished by working in dry boxes filled with argon and by sealing the powders in polyvinyl chloride bags during transfer operations.

After hydrogen cleaning, the powders were cold pressed in graphite dies at pressures of 1920 lb per sq in. and then subsequently vacuum hot pressed at 4000 lb per sq in. and 2100°F for 1 hr. The chamber was evacuated to about 0.5- $\mu$  pressure prior to the start of the heating cycle.

After hot pressing, the billets, which measured 2 in. in diameter by nominally 2 in. long, were skinned of about 1/16 in. on all surfaces and were vacuum canned in mild steel for extrusion. Extrusion was carried out at 2100°F at a reduction ratio of 16 to 1 and at a speed of 200 in. per min.

## RESULTS

The results of microstructural studies of extruded specimens are shown in Table I. Lineal analysis of electron micrographs permitted determination of the vol pct of oxide, the mean free path, and the average oxide particle sizes of all specimens. Each value was determined independently. To determine mean free path, the number of particles per unit length intersected by a random line,  $N_L$ , was determined. Mean free path is then equal to  $(1-f)/N_L$  where  $f$  equals volume fraction of oxide.<sup>7</sup> Vol pct oxide was determined by measuring the total length of random line intercepted by particles,  $A$ , and the total length of random line,  $B$ . Vol pct oxide then equals  $A$  divided by  $B$ .<sup>7</sup> Average oxide particle size was determined by measuring the Martin's Diameter<sup>8</sup> of individual particles and then taking an arithmetic mean of the measured diameters multiplied by  $4/\pi$ .<sup>7</sup> Martin's Diameter is the distance between opposite sides of a particle, measured on a line bisecting the area of the particle. All bisecting lines must be parallel to one another.

Of particular significance here is that the vol pct oxide measured, in some instances, is considerably greater than the amount of MgO added. This conceivably could be due to the method of measurement since etching and other factors could magnify the size of the oxide particles and then increase the observed pct oxide. It is not believed that this accounts for all of the increased oxide content, however; rather it is believed that the general tendency toward an increase of oxide content with decreasing nickel particle size indicates, in some instances, a considerable oxidation of some nickel powders. This hypothesis is supported by the fact that chemical analysis of the cleaned nickel powders indicated nickel oxide contents as high as 2 vol pct immediately after cleaning. Further, after the cleaning operation additional oxidation could have, and probably did, occur during the loading of and subsequent handling of hot-pressing dies. This is believed to be so because the powders are very reactive to oxygen, being pyrophoric in some instances. Fur-

ther, it is known that the dry box in which the work was done was not completely airtight, in spite of reasonable precautions, and in fact, contained up to 2 pct O at the end of the working day, as determined indirectly by chromatographic analysis for  $N_2$ . In addition, observation of microstructures of the nickel specimens, which were made from 1.0-, 0.4-, and 0.2- $\mu$  powders with no oxide additions, indicates a considerable content of a phase that is probably NiO. An example is shown in Fig. 1, which is a nickel specimen prepared from 0.2- $\mu$  nickel powder without MgO addition. In the case of the specimens which contained MgO, this NiO would combine with the MgO because it is mutually soluble in all proportions with the MgO and the result would be an increase in the observed oxide content.

As mentioned, one of the objectives of this study was to achieve particle spacings of MgO in Ni as fine as those in Al- $Al_2O_3$  bodies, that is, less than 1 $\mu$ . Again referring to Table I, it can be noted that such dimensions have been realized with the smallest being about 0.7 $\mu$ . In one case the particle size, 0.06 $\mu$ , was very close to the original particle

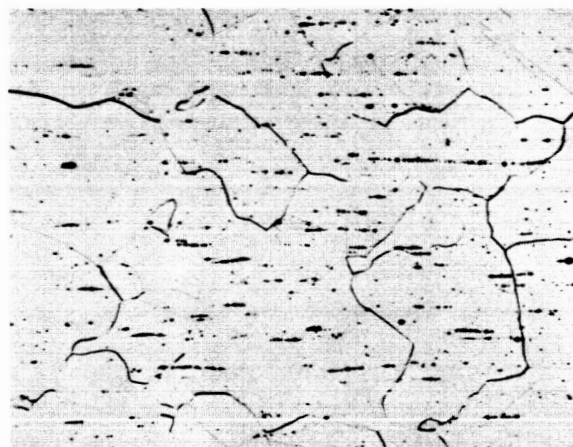


Fig. 1—Nickel oxide in extruded specimen prepared from 0.2 $\mu$  nickel powder with no oxide addition. Etch: 3 lactic acid, 2  $HNO_3$ , 1 HF; X750. Reduced approximately 46 pct for reproduction.

size of the MgO, 0.05 $\mu$ , that was added to the alloys. In this case it can be noted that there was no indica-

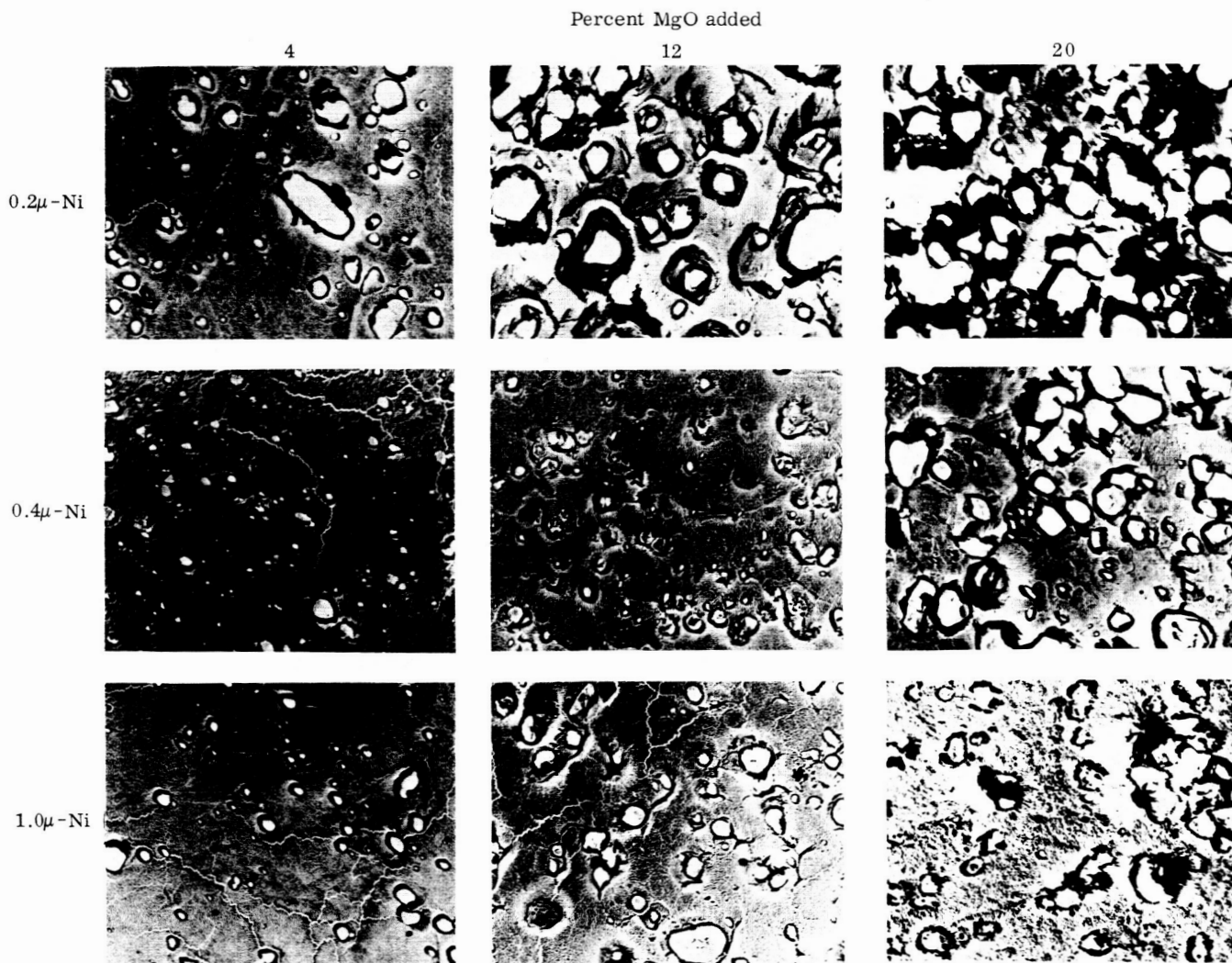


Fig. 2—Effect of initial metallic powder sizes and vol pct of oxides upon as-extruded particle size of oxides MgO. Initial particle size of MgO = 0.05 $\mu$ ; extrusion conditions: temperature, = 2100°F, ratio, = 16 to 1; X15,000. Enlarged approximately 2 pct for reproduction.

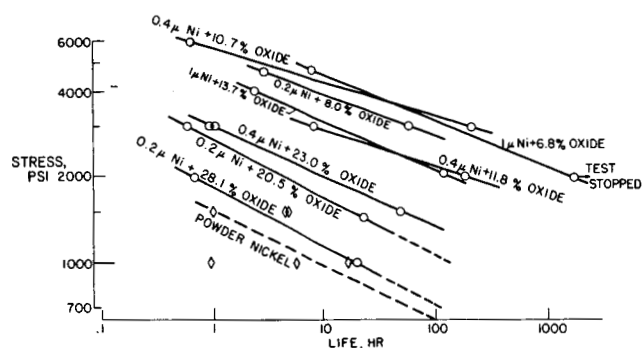


Fig. 3—Stress rupture strength of Ni + MgO dispersion alloys at 1800°F.

tion of oxygen pickup in the body. It was somewhat disappointing that in all the others the oxide phase grew appreciably.

It should also be noted that, in general, particle size increased with increasing vol pct oxide. For example, the specimen with the largest vol pct oxide, 28.1 pct, also had the largest particle size, 0.64μ, and the specimen with the lowest pct oxide, 6.8 pct, had one of the lower particle sizes, 0.20μ.

The growth of the oxide phase can be seen visually in Fig. 2, which presents electron photomicrographs of the bodies at a magnification of 15,000. Note that in general the oxide particle size increases with increasing oxide content and also with decreasing nickel particle size. This subject of oxide agglomeration is treated more extensively in another report.<sup>9</sup>

Fig. 3 shows the stress-rupture properties of these alloys at 1800°F in a helium atmosphere. The helium atmosphere was selected for testing to eliminate the strong influence that oxygen can have on the stress-rupture properties of nickel at this temperature. The strength of the alloys containing oxide dispersions is considerably above that of the powder products containing no oxide. In general, however, it can be noted that when oxides were present, the bodies having lower oxide contents tended to have the greater strength; that strength decreased with increasing oxide content.

## DISCUSSION OF RESULTS

The 100-hr stress-rupture strengths of the alloys of this investigation are compared with the particle size, the vol pct, and the mean free path of the dispersed phase in Figs. 4, 5, and 6, respectively. It should be noted in considering the effect of these parameters on strength that mean free path, particle size, and vol pct oxide are interrelated. Increasing vol pct oxide decreases mean free path for a constant particle size. Decreasing particle size decreases mean free path for a constant vol pct oxide. Also, decreasing particle size allows a decrease in vol pct oxide for a given mean free path. Therefore, one must be careful to consider the variables simultaneously before drawing any conclusion as to the significance of one variable on the properties of the alloys.

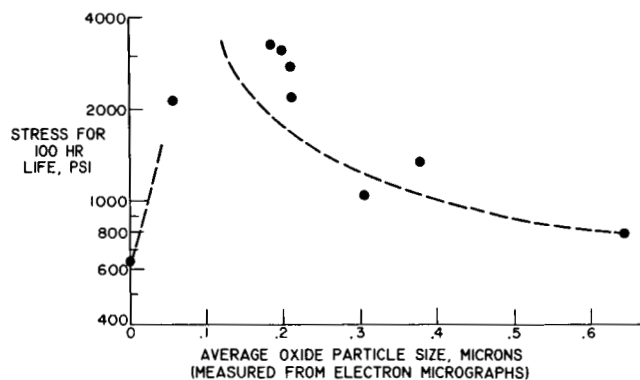


Fig. 4—Relation of particle size, of dispersed MgO, to strength in Ni-MgO dispersed alloys at 1800°F.

In Fig. 4 a comparison of stress for 100-hr stress-rupture life with average particle size of the oxide shows that as particle size decreased the strength increased. Similar results were obtained by Adkins, Sims, and Jaffee,<sup>10</sup> who found that stress-rupture strengths at 500°C of cobalt alloys increased as finer oxide dispersoids were added to the alloys. It is generally agreed that finer particle sizes should give better stress-rupture strengths, but the reasoning is generally associated with the effect of particle size on the mean free path, that is, the mean free path decreases with decreasing particle size for a given vol pct oxide and that the significant parameter is mean free path. It will be shown subsequently that even though strength was related to particle size, mean free path was not a significant parameter for the alloys studied in this investigation.

Fig. 5 compares measured vol pct oxide with stress for 100-hr rupture life. Strength decreased with increasing vol pct oxide in the range of oxide contents studied, from 7 to 28 pct. Further, in this case there obviously is an optimum vol pct of oxide somewhere between 0 and 7 pct. Optimum vol percentages of oxide have been observed to occur in other dispersion-strengthened products. For example, in a Cu-Al<sub>2</sub>O<sub>3</sub> alloy, Zwilsky and Grant<sup>11</sup> found that an optimum tensile strength occurred at approximately 7 pct and that increasing the oxide

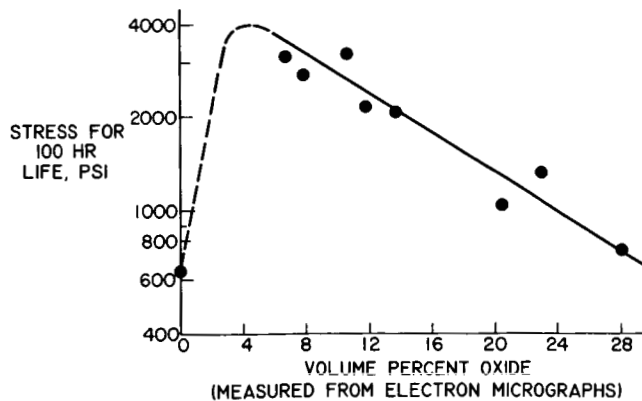


Fig. 5—Relation of vol pct oxide to strength, in Ni-MgO dispersed alloys, at 1800°F

content caused a reduction in strength. The original dispersion-strengthened aluminum-aluminum oxide materials created by Irmann, however, exhibited steadily increasing strengths with increasing vol pct oxides although the rate of increase began to diminish as more oxide was added.

In Fig. 6 stress for 100-hr stress-rupture life is plotted vs reciprocal mean free path. It can be noted that the effect of increasing stress-rupture strength with decreasing mean free path was not observed in the range of mean free paths investigated herein, all of which were less than  $2\mu$  (reciprocal of greater than 0.5). In fact, it may be seen that a well defined relation between mean free path and strength is not evident. In view of the Cremens and Grant data mentioned previously,<sup>5</sup> it might be expected that stress-rupture strength would increase with a decrease in the mean free path. On the other hand, there are occasions when stress-rupture strength does not increase with a decrease in mean free path. For example, Grant and Preston<sup>12</sup> have noted that, in Al-Al<sub>2</sub>O<sub>3</sub> SAP alloys, if stress for 100-hr rupture life is plotted vs mean free path, the slopes of the lines relating strength to mean free path level off with increasing test temperatures. Since the stress-rupture tests of this study were run at 1800°F while the tests of Cremens and Grant were run at 1500°F a leveling off of a strength-mean free path curve might have been expected. It would not, however, be expected that the data would have the scatter that is noted in Fig. 6. Thus one is led to look for another explanation for this lack of correlation.

Further considering the data, it is significant that some oxide addition was very beneficial to strength. On the other hand, too much oxide addition contributed little if anything to the 100-hr stress-rupture strength of nickel. Further, in the range of oxide additions studied, mean free path was evidently not related to strength. Finally, strength was considerably greater for fine particle sizes than for coarse particle sizes.

Whether fine particle size is or is not the important parameter for strengthening is questionable. The reason for this is that the variables of particle size and vol pct oxide were, as was noted previously, in general, proportional to one another in the alloys studied in this investigation, see Table I.

There is reason to believe, however, that the vol pct of oxide is the most significant factor relating to the strength of these alloys. The following postulate is offered as a likely explanation for the results: The decrease in strength with increasing vol pct oxide may be related to the interaction of impurities in the matrix and/or the impurities in the MgO with the NiO that was picked up during various stages of handling. As more oxide was added or finer nickel was used, more impurities became available. Thus, for example, C and H, which might have been adsorbed during the grinding of the MgO, and C and H and NiO associated with the nickel could react to form such gases as CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>O vapor during any high-temperature

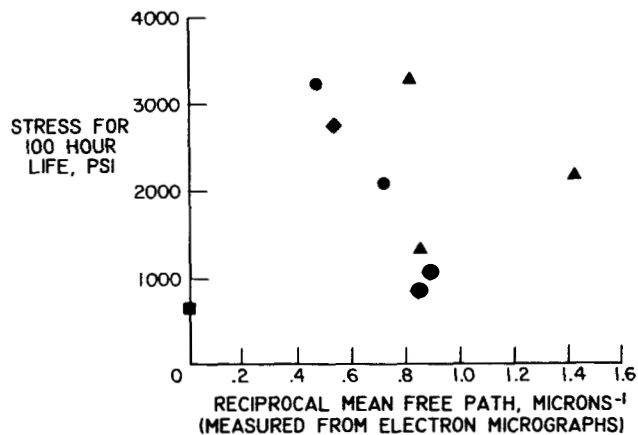


Fig. 6—Relation of mean free path to strength in Ni-Mgo dispersion alloys at 1800°F.

operation or test. This could give rise to gas pockets at the metal-oxide interfaces, which could be the cause of weakness and failure in stress-rupture testing.

Annealing of extruded specimens, at a temperature of 2100°F for 16 hr showed metallographically that pores did develop in some of the alloys around the oxide particles and that the pores were larger and more numerous as the amount of oxide in the alloys was increased. This may be a somewhat similar phenomenon to that observed by Cremens, Bryan, and Grant<sup>13</sup> on aluminum-aluminum oxide SAP alloys which were heated at very high temperatures relative to the melting point of aluminum. These heat treatments produced what was thought to be gas pockets. It should be noted, however, that when gas pockets formed in the aluminum-aluminum oxide system they did so very near the melting point of aluminum; while in this study the gas pockets formed at 2100°F, a temperature well below the melting point of nickel. This would suggest that the gas pressures in the alloys studied in this investigation were much higher than they were in the aluminum-aluminum oxide alloys and that gas pressure around oxide particles could contribute to the weakness of the specimens. In a stress-rupture test this tendency to form voids around oxide particles could lead to the early failure of the specimen through the movement of vacancies to the voids at the oxide-metal interfaces and to related dislocation movement. Ultimately the voids could grow by diffusion of vacancies and could grow large enough to become interconnected, thereby forming incipient cracks. Thus, these considerations could explain why the alloys of this study behaved differently from Ni-Al<sub>2</sub>O<sub>3</sub> SAP alloys,<sup>5</sup> which increased in strength with decreasing mean free path, and why they decreased in strength with decreasing vol pct oxide. It would also indicate that, very possibly, the relation of stress-rupture strength to particle size is subordinate to the impurity situation in the alloys.

It is interesting to speculate at this point on the effect of impurities in other metal-oxide alloys that will be prepared in the future. It is possible that

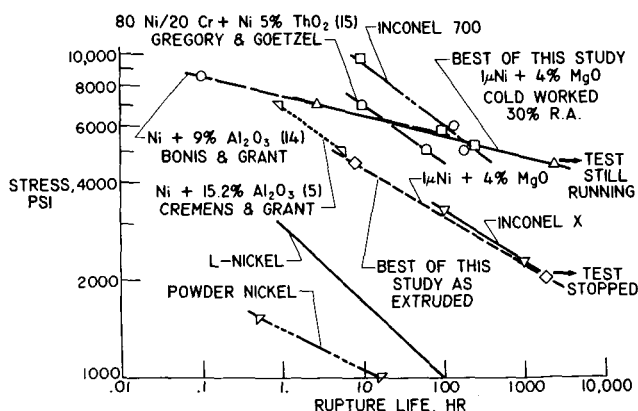


Fig. 7—A comparison of stress rupture strength of several Ni alloys.

the properties of these alloys might be considerably enhanced by the removal of impurities from both oxides and metal matrices. In any case, it is certain that a better understanding of dispersion-strengthened alloys could be reached if efforts to decrease impurity contents would be pursued.

Fig. 7 compares the strength of the best of the alloys of this study with other Ni-SAP type alloys and with two commercial nickel alloys. The strength of the best of the alloys of this investigation is much better than that of pure nickel, but is only fair when compared with the nickel alloys, Inconel X, and Inconel 700.

Since it was felt that cold working of this alloy might be beneficial, the best alloy was cold rolled to 30 pct reduction in area and thereby a large increase in the stress-rupture strength was noted. It is interesting that this alloy in the cold-worked condition has almost identical properties to a nickel plus 9 vol pct  $\text{Al}_2\text{O}_3$  alloy prepared by Bonis and Grant.<sup>14</sup>

## CONCLUDING REMARKS

As a result of this study it was found possible to achieve dispersions of MgO in nickel of a fineness or mean free path comparable to that of SAP. This is the first time to our knowledge that such fine dispersions have been achieved by the mechanical mixing technique. A significant factor that permitted the achievement of such fine dispersions was the use of nickel powders of less than  $1\mu$  particle size—achieved by ball milling.

In one case the initial particle size of the MgO powder,  $0.05\mu$ , was retained during processing from powder to extruded bodies. It was somewhat disappointing, however, to note that in general the MgO particles grew very rapidly during processing. It is believed that a significant factor in causing MgO particle growth was the fact that the oxide content of the bodies increased during processing even though reasonable precautions were taken to avoid oxygen contamination of the powders. Thus, the particles measured are undoubtedly in part NiO as well as MgO. These data would indicate that extremely careful techniques may, in some cases, be required to avoid oxidation of the powders during processing and concomitant growth of the dispersed oxide phase.

It was also shown that in these alloys the  $1800^\circ\text{F}$  stress-rupture strength improvement over unalloyed nickel was greatest for low oxide additions and decreased as the oxide content increased. This relation indicates that the oxide (with concurrent impurity oxides that were obtained during processing) at some level become a source of weakness rather than of strength.

Finally, cold working significantly increased the strength of the best of these alloys and made it equivalent in strength at  $1800^\circ\text{F}$  to the best reported nickel plus oxide alloys made with mechanical mixing techniques.

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